Revised 2/21/96

INDIANA DEPARTMENT OF TRANSPORTATION
MATERIALS AND TESTS DIVISION

MERCAPTANS (WATER INSOLUBLE) BY IODIMETRIC TITRATION-DEADSTOP
ITM No. 602-89T

1.0 SCOPE

1.1 This method involves the iodimetric oxidation of the primary mercaptan group to the disulfide:

2 RSH (primary) = I2 ----------> RSSR + 2 HI

The endpoint is detected by a deadstop procedure using as titrant a solution of iodine in benzene. A solvent system of pyridine-benzene is used to dissolve the sample and iodide in water initiates the electrode response.

2.0 REAGENTS

2.1 Standard 0.05 N Iodine in Benzene

2.2 Benzene, Reagent Grade

2.3 Pyridine, Reagent Grade

2.4 Potassium Iodide, (Iodate Free), Reagent Grade

3.0 APPARATUS

3.1 Buret, 25 mL, self-leveling type preferred

3.2 Beaker, wide mount, 250 mL

3.3 Karl Fisher Titration assembly or equivalent with single dual platinum electrode. Electrode is obtainable from Precision Scientific Co., 3737 W. Cortland Street, Chicago 47, Illinois, or with tapered joint from Arthur H. Thomas Co., vine at Third, P.O. Box 779, Philadelphia 5, Pennsylvania.

3.4 Magnetic stirrer and teflon covered stirring bar

3.5 Balance, capable of determining the mass up to 160 g to 0.01 g accuracy

3.6 Miscellaneous laboratory equipment, as required

4.0 PROCEDURE

4.1 Add 100 mL (graduate) of a 60/40 (by volume) pyridine-benzene solution to a 250 mL beaker.

4.2 Add 10 mL (graduate) 2% aqueous potassium iodide solution.

4.3 Insert dual platinum electrode into solution leaving space for magnetic stirrer.

4.4 Set sensitivity of titration assembly microammeter to desired level by titration with 0.05 N I2 in benzene. (See Supplementary Information)

4.5 Add to the test solution a sample of 0.5 g ± 0.1 g. The sample size is determined by weighing a shell vial containing the material to be analyzed, pouring a small amount into the test solution, and reweighing the shell vial.

4.6 Refill the buret to capacity with 0.05 N I_2 in benzene. Titrate the test solution to the microammeter reading previously established in step 4.4 above, using magnetic stirrer. As the endpoint is approached, the test solution will appear to change from a clear condition to a yellowish tint. The microammeter needle may momentarily exceed the target setting, but will return to it upon the addition of another drop or two of titrant. Should gross over-titration occur, add another 0.5 g. sample to the test solution and retitrate, using the combined sample masses as a calculations base.

4.7 Record mL of 0.05 N I_2 consumed.

5.0 SUPPLEMENTARY INFORMATION

5.1 To adjust the microammeter to a proper sensitivity of needle response, a sufficient amount of 0.05 N I_2 in benzene is titrated into the test solution (step 4.4 above) to yield a reading of about 15 µA. To avoid a condition of excessive circuit resistance, the amount of I_2 solution added at this point should not exceed 0.4 mL.

5.2 At the beginning of step 4.4 above, the electrodes are in a polarized condition and current flow is impeded. With the addition of a small amount of iodine, the electrodes are depolarized and current flow registers on the ammeter. Upon addition of the sample, electrode polarization again occurs and current flow is impeded until introduction of an excess of iodine results in electrode depolarization at the preselected end point.

5.3 The solvent system shall contain water with potassium iodide otherwise no electrode response will occur or erratic meter needle fluctuations are encountered.

5.4 Any of the various types of pH meters which have a built in polarizing circuit are adaptable to the present procedure. Similar results were obtained by use of the Leeds & Northrup Model No. 7664-A1, Beckman Zeromatic and Fisher Titrimeter Model No. 35. The simple circuit diagrammed in aquametry by Mitchell and Smith may be used. A schematic of the apparatus is appended.

5.5 No more than 2 consecutive determinations should be run in each solvent system.

6.0 CALCULATION

6.1 Calculate % SH:

$$\% \text{ SH} = \frac{(\text{mL } I_2)\ (\text{N } I_2)\ (3.31)}{\text{g sample}}$$

6.2 Report results to the nearest 0.01% in the range 0-20%; above 20%, report results to the nearest 0.1%. Limited data indicate the precision to be on the order of ± 0.3% relative.